Diffusion Through Swelling Membranes with a Robin Boundary Condition

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ABSTRACT: A Robin boundary condition at the downstream surface of stretched membrane is used to study diffusion through swollen polymer membranes. Four dimensionless parameters are used to describe the diffusion process. These parameters are associated with the effect of swelling, relaxation, and retardation times of the polymer matrix as well as the normal derivative condition at the downstream side of the membrane. The effect of these four parameters is discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 47–51, 2008

Key words: diffusion; swelling; membranes; stress

INTRODUCTION

In a recent paper, Liu et al.[1] discussed mass transport through swelling membranes. In that paper the concentration at the downstream side of the membrane was assumed to be zero. However, as in the case of geomembranes (landfill liners for example), the pollutants seep into another medium.[2–4] An appropriate boundary condition for such a case is that the concentration gradient is proportional to the concentration at the downstream side of the membrane.[5]

MATHEMATICAL FORMULATION AND SOLUTION

We start with the nondimensional form in Liu et al.[1]

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} + \gamma_1 \frac{\partial^2 \sigma}{\partial x^2} \tag{1}$$

$$\gamma_2 \frac{\partial \sigma}{\partial t} + \sigma = c + \gamma_3 \frac{\partial c}{\partial t} \tag{2}$$

where c and σ refer to permeant concentration and stress on the polymer membrane, respectively. The dimensionless parameters $\gamma_1, \gamma_2, \gamma_3$ are defined as follows[1]

$$\gamma_1 = E\nu/D, \quad \gamma_2 = \frac{\beta_1}{(L^2/D)}, \quad \gamma_3 = \frac{\beta_2}{(L^2/D)} \tag{3}$$

where D is the molecular diffusion coefficient, E is a stress-driven (elastic) diffusion coefficient, β_1 is a relaxation time, and β_2 is a retardation time (expressed in a Jeffreys' type model[1]). The parameter ν relates the equilibrium stress with the concentration of the solvent.

The initial and boundary conditions are

$$\begin{aligned} &c(x,0) = 0, \\ &\sigma(x,0) = 0, \\ &c(0,t) = 1, \\ &\frac{\partial c}{\partial x}(1,t) = \alpha c(1,t), \quad \alpha < 0 \end{aligned} \tag{4}$$

Eliminating σ from eqs. (1) and (2), yields

$$\frac{\partial^2 c}{\partial t^2} + \frac{1}{\gamma_2}\frac{\partial c}{\partial t} = \frac{\gamma_2 + \gamma_1\gamma_3}{\gamma_2}\frac{\partial^3 c}{\partial t \partial x^2} + \frac{1+\gamma_1}{\gamma_2}\frac{\partial^2 c}{\partial x^2} \tag{5}$$

Assuming $c = X(x)T(t)$ and using the separation of variables method, we obtain

$$\frac{\gamma_2 T'' + T'}{(1+\gamma_1)T + (\gamma_2 + \gamma_1\gamma_3)T'} = \frac{X''}{X} = -\eta^2 \tag{6}$$

where η is a parameter. For $\eta = 0$, the appropriate solution satisfying the boundary conditions is

$$X_0 = 1 + \frac{\alpha}{1-\alpha}x, \quad T = 1, \quad \alpha < 0 \tag{7}$$

We assume that $X_\eta(0) = 0$ and $X'_\eta(1) = \alpha X_\eta(1)$ for other (nontrivial) values of the parameter η. Thus, $\eta = \eta_s$, $s = 1, 2, \ldots$ $X_s \propto \sin \eta_s x$, and $T_s = A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}$, where η_s are the roots of the transcendental equation

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$$\alpha \tan \eta = \eta \tag{8}$$

thus,

$$X_s T_s = [A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}] \sin \eta_s x \tag{9}$$

with

$$\lambda_{1,2}(s) = \frac{\left[W \pm \sqrt{W^2 - 4\eta_s^2 \gamma_2 (1+\gamma_1)}\right]}{2\gamma_2} \tag{10}$$

and

$$W = 1 + \eta_s^2(\gamma_2 + \gamma_1\gamma_3) \tag{11}$$

Note that the characteristic functions $\sin \eta_s x$ are orthogonal. The complete solution for c is then given by

$$c(x,t) = 1 + \frac{\alpha}{1-\alpha}x + \sum_{s=1}^{\infty}[A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}] \sin \eta_s x \tag{12}$$

Using the orthogonality of $\sin \eta_s x$ and the initial condition, we have

$$A_s + B_s = -\frac{2(\alpha^2 + \eta_s^2)}{\eta_s(\alpha^2 + \eta_s^2 - \alpha)} \tag{13}$$

We need one more relation between A_s and B_s in order to completely determine the solution. This relation is obtained by solving for σ, using eqs. (2) and (12), and then insuring compatibility of the solutions for c and σ with respect to eq. (1). Equation (2) can be expressed as

$$\gamma_2 \frac{\partial}{\partial t}\left(\sigma e^{\frac{t}{\gamma_2}}\right) = \left(c + \gamma_3 \frac{\partial c}{\partial t}\right) e^{\frac{t}{\gamma_2}} \tag{14}$$

Using eq. (12), the solution for eq. (14) is

$$\sigma = \left(1 + \frac{\alpha}{1-\alpha}x\right)\left(1 - e^{-\frac{t}{\gamma_2}}\right) + \sum_{s=1}^{\infty}\left[\begin{array}{l} \frac{1-\lambda_1\gamma_3}{1-\lambda_1\gamma_2}A_s e^{-\lambda_1(s)t} + \frac{1-\lambda_2\gamma_3}{1-\lambda_2\gamma_2}B_s e^{-\lambda_2(s)t} \\ -\left\{\frac{1-\lambda_1\gamma_3}{1-\lambda_1\gamma_2}A_s + \frac{1-\lambda_2\gamma_3}{1-\lambda_2\gamma_2}B_s\right\}e^{-\frac{t}{\gamma_2}} \end{array}\right] \sin \eta_s x \tag{15}$$

Combining eqs. (1), (12), and (15), we obtain

$$\frac{1-\lambda_1\gamma_3}{1-\lambda_1\gamma_2}A_s + \frac{1-\lambda_2\gamma_3}{1-\lambda_2\gamma_2}B_s = 0 \tag{16}$$

and eq. (15) reduces to

$$\sigma = \left(1 + \frac{\alpha}{1-\alpha}x\right)\left(1 - e^{-\frac{t}{\gamma_2}}\right) + \sum_{s=1}^{\infty}\left[\frac{1-\lambda_1\gamma_3}{1-\lambda_1\gamma_2}A_s e^{-\lambda_1(s)t} + \frac{1-\lambda_2\gamma_3}{1-\lambda_2\gamma_2}B_s e^{-\lambda_2(s)t}\right] \sin \eta_s x \tag{17}$$

Via eqs. (13) and (16), we determine

$$\begin{aligned} A_s &= \frac{2(1-\lambda_2\gamma_3)(1-\lambda_1\gamma_2)(\alpha^2+\eta_s^2)}{\eta_s(\alpha^2+\eta_s^2-\alpha)(\lambda_1-\lambda_2)(\gamma_2-\gamma_3)} \\ B_s &= -\frac{2(1-\lambda_2\gamma_2)(1-\lambda_1\gamma_3)(\alpha^2+\eta_s^2)}{\eta_s(\alpha^2+\eta_s^2-\alpha)(\lambda_1-\lambda_2)(\gamma_2-\gamma_3)} \end{aligned} \tag{18}$$

The expressions for $c(x,t)$ and $\sigma(x,t)$ are given by eqs. (12), (15), and (16).

Clearly the stress remains finite at equilibrium. The dimensionless form of the flux F* at $x^* = 1$ is given by

$$F^* = -\left[\frac{\partial c^*}{\partial x^*} + \gamma_1 \frac{\partial \sigma^*}{\partial x^*}\right]_{x^*=1} = -\frac{\alpha}{1-\alpha}\left(1 + \gamma_1 - \gamma_1 e^{-\frac{t^*}{\gamma_2}}\right) - \sum_{s=1}^{\infty}\left[\begin{array}{l} \frac{(1-\lambda_2\gamma_3)(1+\gamma_1-\lambda_1(\gamma_2+\gamma_1\gamma_3))(\alpha^2+\eta_s^2)}{(\alpha^2+\eta_s^2-\alpha)(\lambda_1-\lambda_2)(\gamma_2-\gamma_3)}e^{-\lambda_1(s)t^*} \\ -\frac{(1-\lambda_1\gamma_3)(1+\gamma_1-\lambda_2(\gamma_2+\gamma_1\gamma_3))(\alpha^2+\eta_s^2)}{(\alpha^2+\eta_s^2-\alpha)(\lambda_1-\lambda_2)(\gamma_2-\gamma_3)}e^{-\lambda_2(s)t^*} \end{array}\right] \cos \eta_s \tag{19}$$

In dimensional form eq. (19) becomes

$$\frac{\mathrm{LF}}{\rho D c_s} = -\frac{\alpha}{1-\alpha}\left(1 + \gamma_1 - \gamma_1 e^{-\frac{Dt}{L^2\gamma_2}}\right) - \sum_{s=1}^{\infty}\left[\begin{array}{l} \frac{(1-\lambda_2\gamma_3)(1+\gamma_1-\lambda_1(\gamma_2+\gamma_1\gamma_3))(\alpha^2+\eta_s^2)}{(\alpha^2+\eta_s^2-\alpha)(\lambda_1-\lambda_2)(\gamma_2-\gamma_3)}e^{-\lambda_1(s)\frac{Dt}{L^2}} \\ -\frac{(1-\lambda_1\gamma_3)(1+\gamma_1-\lambda_2(\gamma_2+\gamma_1\gamma_3))(\alpha^2+\eta_s^2)}{(\alpha^2+\eta_s^2-\alpha)(\lambda_1-\lambda_2)(\gamma_2-\gamma_3)}e^{-\lambda_2(s)\frac{Dt}{L^2}} \end{array}\right] \cos \eta_s \tag{20}$$

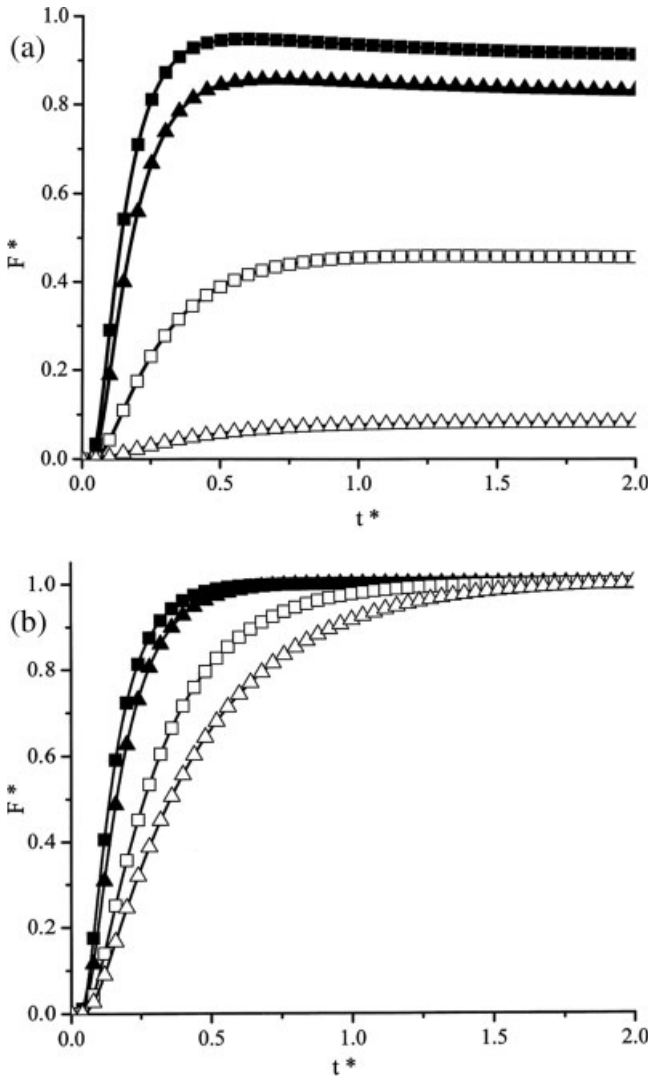

Figure 1 Effect of α on the diffusion process ($\gamma_1 = 0, \gamma_2 = 1, \gamma_3 = 0$): (■), $\alpha = -\infty$; (▲), $\alpha = -10$; (□), $\alpha = -1$; (△), $\alpha = -0.1$.

Note that the results for the paper by Liu et al.[1] can be obtained for the limiting case where c becomes zero at $x^* = 1$, which corresponds to the (mathematical) limiting case $\alpha = -\infty$.

DISCUSSION

As discussed by Liu et al.,[1] $\gamma_1, \gamma_2, \gamma_3$ relate to the swelling of the polymer matrix. The magnitude of the negative variable γ_1 is associated with the effect of the polymer relaxation on the diffusion process. Parameter γ_2 is a dimensionless time, which relates to the rate of polymer relaxation. A second dimensionless time γ_3, is associated with the polymer retardation rate. The model considers not only diffusion of a specific solvent into a polymer membrane, but also interactions between the solvent and the polymer.

In this contribution, a Robin boundary condition is used to better simulate conditions that would prevail in the case of solvent diffusion through geomembranes.[4–6] The Robin boundary condition includes an important variable α. Figure 1(a) shows the effect of α on the dimensionless flux versus dimensionless time profile predicted by eq. (19). The values of the variables $\gamma_1 = 0, \gamma_2 = 1, \gamma_3 = 0$ represent a Fickian diffusion process. Note that eq. (8) is used to determine η_s when α is set. Figure 1(a) illustrates that the steady state flux decreases with increasing (decreasing in magnitude) α. As $\alpha \to 0, F^* \to 0$ and as $\alpha \to -\infty, F^* \to 1$. According to the boundary condition, eq. (4), $-1/\alpha$ can be treated as a resistance for penetrant diffusion from the downstream side of the membrane into the environment. As $\alpha \to 0$, the resistance $-1/\alpha$ is infinite; that is: no penetrant can diffuse across the membrane downstream boundary. This corresponds to a zero flux. As $\alpha \to -\infty$ (i.e. zero resistance), all penetrant reaching the downstream side of the membrane enters the environment. Figure 1(b) shows the normalization of flux under the same conditions as Figure 1(a). As the magnitude of α decreases, (corresponding to a larger resistance $-1/\alpha$), more time is needed to reach steady state.

Figure 2 shows the concentration distribution profile for a specific case where $\gamma_1 = -0.1, \gamma_2 = 1, \gamma_3 = 0, \alpha = -0.1$. As the nondimensional time t^* increases, the concentration at the membrane downstream boundary $c^*(1, t^*)$ increases to attain a steady concentration. According to eq. (12), as

$$t^* \to \infty, \quad c^*(x^*, t^*) = 1 + \frac{\alpha}{1 - \alpha} x^* \tag{21}$$

which is a linear distribution, as illustrated in Figure 2. When $\alpha \to 0$ and $t^* \to \infty$, $c^*(x^*, t^*) \to 1$. When $\alpha = -\infty$ and $t^* \to \infty$, $c^*(1, t^*) = 0$, which is the case discussed in Liu et al.[1]

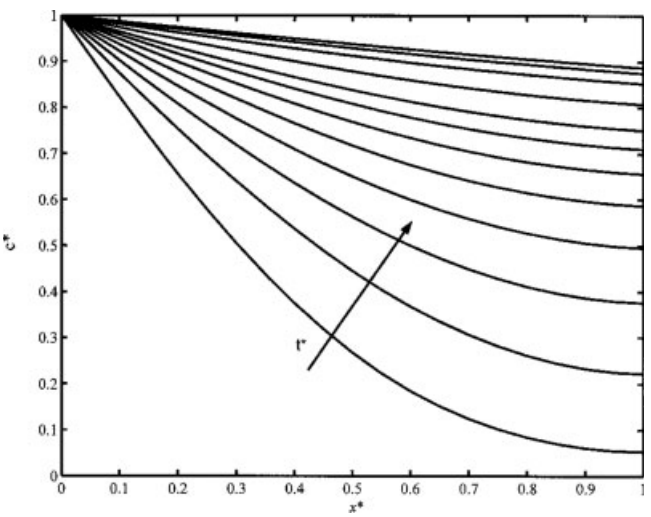

Figure 2 Concentration distribution profiles for ($\gamma_1 = -0.1, \gamma_2 = 1, \gamma_3 = 0, \alpha = -0.1$).

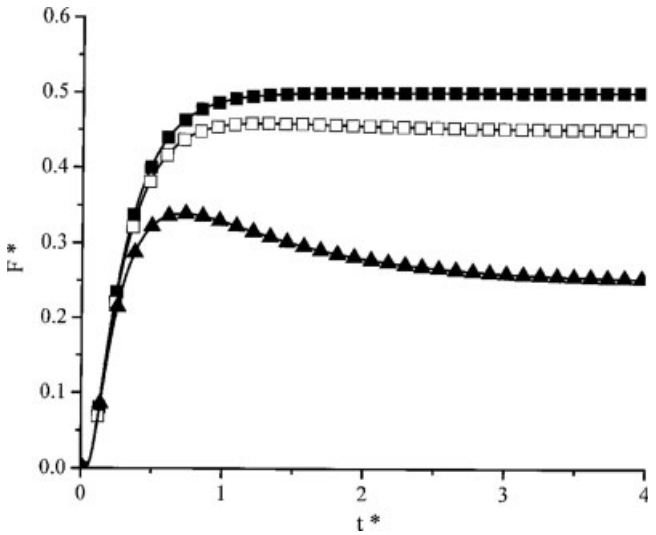

Figure 3 Effect of γ_1 on the diffusion process ($\gamma_2 = 1, \gamma_3 = 0, \alpha = -1$): (■), $\gamma_1 = 0$; (□), $\gamma_1 = -0.1$; (▲), $\gamma_1 = -0.5$.

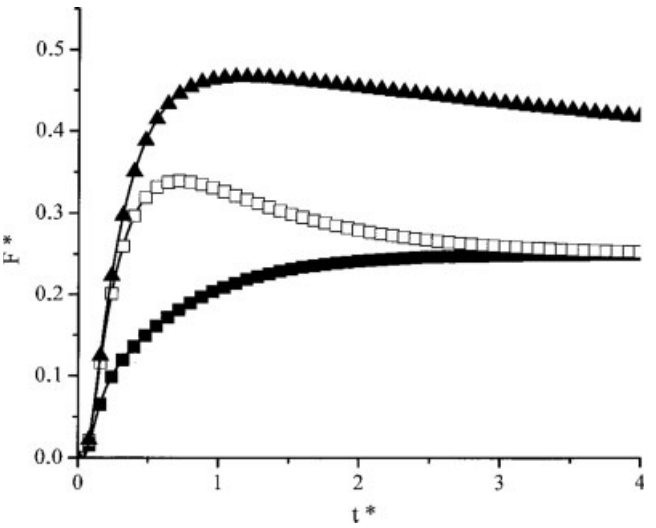

Figure 4 Effect of γ_2 on the diffusion process ($\gamma_1 = -0.5, \gamma_3 = 0, \alpha = -1$): (■), $\gamma_2 = 0.1$; (□), $\gamma_2 = 1$; (▲), $\gamma_2 = 10$.

Figure 3 shows the effect of γ_1 on the flux versus time profile. As previously discussed,[1,7] γ_1 is associated with the effect of polymer swelling on the diffusion process. To show the significant role of γ_1, we choose $\gamma_2 = 1, \gamma_3 = 0, \alpha = -1$. When $\gamma_1 = 0$, (swelling has no effect on diffusion), one recovers Fickian diffusion. As γ_1 decreases (increase in the magnitude of γ_1), polymer swelling (polymer relaxation) gains importance. The diffusion process becomes non-Fickian, as shown in Figure 3, where $\gamma_1 = -0.5$. A significant overshoot appears in the flux profile. Another aspect of the effect of γ_1 is that it decreases the steady state flux. This corresponds to a negative convective flux as a result of polymer swelling.

The effect of γ_2 on the prediction of the flux is shown in Figure 4. We choose $\gamma_1 = -0.5, \gamma_3 = 0$, $\alpha = -1$ to clearly show the importance of γ_2. This variable, which is a dimensionless time, similar to the Deborah number *De* in Ref. 8–10, relates to the rate of polymer relaxation. When γ_2 is very small (polymer chain relaxation is substantially faster than the diffusion time scale), the diffusion approaches Fickian diffusion (■ in Fig. 4). When γ_2 is of order one (the polymer relaxation time is of the same order of magnitude as the diffusion time), polymer structural arrangements accompany the diffusion process. This results in an overshoot in the flux profile. The non-Fickian behavior is shown as (□ in Fig. 4). When γ_2 is very large (the relaxation time is less than the diffusion time), the relaxation of the polymer may not be able to affect the diffusion process at short times, again generating Fickian like behavior. However, at longer times, the flux will decrease due to the negative convective flux caused by polymer swelling. As shown in Figure 4 [▲], the flux approaches Fickian behavior at short times.

The other dimensionless time γ_3 is associated with a polymer retardation time,[1,7] related to creep behavior.[11,12] Thus, γ_3 is a time scale associated with the swelling process, whereas γ_2, is associated with the relaxation process. As shown in Figure 5, when γ_3 increases (the swelling process takes more time), the

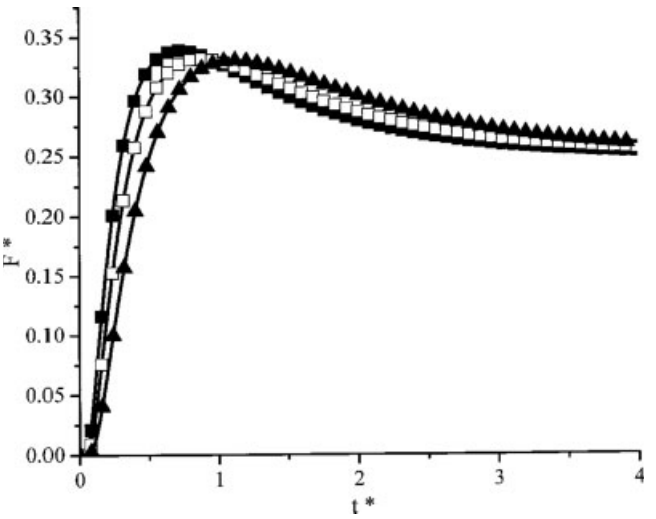

Figure 5 Effect of γ_3 on the diffusion process ($\gamma_1 = -0.5, \gamma_2 = 1, \alpha = -1$): (■), $\gamma_3 = 0$; (□), $\gamma_3 = 0.4$; (▲), $\gamma_3 = 0.8$.

flux curves shifts to the right, reflecting the longer time required to reach steady state.

In summary, we developed a model to study mass transport through swelling polymer membranes via a Robin boundary condition. Four dimensionless parameters, associated with polymer swelling, relaxation/retardation times, and resistance to diffusion from the downstream side of the membrane, are used to describe the diffusion process.

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